

CLAIMS

Having thus described our invention, what we claim as new, and desire to secure by Letters Patent is:

1. A liquid oligomeric composition comprising:
a multifunctional mercaptan; and
an organic soluble, ungelled, uncrosslinked, Michael addition polyacrylate reaction product.
2. The liquid oligomeric composition, according to claim 1, wherein said Michael addition polyacrylate product is formed from a multifunctional acrylate Michael acceptor and a β -dicarbonyl Michael donor.
3. The liquid oligomeric composition, according to claim 1, wherein said β -dicarbonyl Michael donor is selected from the group consisting of β -keto esters, β -diketones, β -ketoamides, β -ketoanilides, and mixtures thereof.
4. The liquid oligomeric composition, according to claim 1, wherein said multifunctional acrylate Michael acceptor is selected from the group consisting of diacrylates, triacrylates, and tetraacrylates.
5. The liquid oligomeric composition, according to claim 1, wherein said β -dicarbonyl Michael donor is a β -diketone or a β -ketoester.
6. The liquid oligomeric composition, according to claim 3, wherein said β -dicarbonyl has equivalent functionality (N) wherein $N = 2, 4, 6, \text{ or } 8$.

7. The liquid oligomeric composition, according to claim 4, wherein the molar acrylic functional group ratio of said diacrylate Michael acceptor to said β -dicarbonyl donor is:
 - $\geq 1:1$ where said β -dicarbonyl functionality=2,
 - $\geq 4.5:1$ where said β -dicarbonyl functionality=4,
 - $\geq 4.5:1$ where said β -dicarbonyl functionality=6, and
 - $\geq 3.5:1$ where said β -dicarbonyl functionality=8.
8. The liquid oligomeric composition, according to claim 4, wherein the molar acrylic functional group ratio of said triacrylate Michael acceptor to said β -dicarbonyl donor is:
 - $\geq 2:1$ where said β -dicarbonyl functionality=2,
 - $\geq 6.4:1$ where said β -dicarbonyl functionality=4,
 - $\geq 7.8:1$ where said β -dicarbonyl functionality=6, and
 - $\geq 7.4:1$ where said β -dicarbonyl functionality=8.
9. The liquid oligomeric composition, according to claim 4, wherein the molar acrylic functional group ratio of said tetraacrylate Michael acceptor to said β -dicarbonyl donor is:
 - ≥ 3.3 where said acetoacetate functionality=2,
 - $\geq 12.3:1$ where said β -dicarbonyl functionality=4,
 - $\geq 13.2:1$ where said β -dicarbonyl functionality=6, and
 - $\geq 12.7:1$ where said β -dicarbonyl functionality=8.
10. The liquid oligomeric composition, according to claim 1, wherein said mercaptan has at least two thiol groups.
11. The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a dimercaptan.

12. The liquid oligomeric composition, according to claim 11, wherein said dimercaptan is selected from the group consisting of

ethylene glycol dimercaptopropionate,
diethylene glycol dimercaptopropionate,
4-t-butyl-1, 2-benzenedithiol,
bis-(2-mercaptoethyl) sulfide,
4, 4'-thiodibenzenethiol,
benzenedithiol,
glycol dimercaptoacetate,
glycol dimercaptopropionate ethylene bis (3-mercaptopropionate),
polyethylene glycol dimercaptoacetates,
polyethylene glycol di (3-mercaptopropionates),
2, 2-bis (mercaptomethyl)-1, 3-propanedithiol,
2, 5-dimercaptomethyl-1, 4-dithiane,
bisphenofluorene bis (ethoxy-3-mercaptopropionate),
4, 8-bis (mercaptomethyl)-3, 6, 9-trithia-1, 11-undecanedithiol,
2-mercaptomethyl-2-methyl-1, 3-propanedithiol,
1, 8-dimercapto-3, 6-dioxaoctane, and
thioglycerol bismercapto-acetate.

13. The liquid oligomeric composition, according to claim 11, wherein a preferred di-functional mercaptan is ethylene glycol dimercaptopropionate.

14. The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a trimercaptan.

15. The liquid oligomeric composition, according to claim 14, wherein said trimercaptan is selected from the group consisting of

trimethylol propane (tris-mercaptopropionate) (TMPTMP),
trimethylolpropane tris (3-mercaptopropionate),
trimethylolpropane tris (3-mercaptoacetate),
Tris-(3-mercaptopropyl) isocyanurate, 1, 2, 3-trimercaptopropane,
dipentaerythrithiol,
1, 2, 4-trimercaptomethyl benzene, and

tris(3-mercaptopropionate)triethyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione.

16. The liquid oligomeric composition, according to claim 14, wherein a preferred tri-functional mercaptan is trimethylol propane (tris-mercaptopropionate) (TMPTMP).

17. The liquid oligomeric composition, according to claim 1, wherein said mercaptan is a polyfunctional mercaptan.

18. The liquid oligomeric composition, according to claim 17, wherein said polyfunctional mercaptan is selected from the group consisting of

Poly (mercaptopropyl methyl) siloxane (PMPMS),
4-mercaptopomethyl-3, 6-dithia-1, 8-octanedithiolpentaerythritol tetrakis (3-mercaptopacetate), and
pentaerythritol tetrakis (3-mercaptopropionate).

19. The liquid oligomeric composition, according to claim 17, wherein a preferred polyfunctional mercaptan is poly (mercaptopropyl methyl) siloxane (PMPMS).

20. The liquid oligomeric composition, according to claim 1, wherein said Michael addition reaction is carried out in the presence of a strong base.

21. The liquid oligomeric composition, according to claim 20, wherein said base is chosen from the group consisting of cyclic amidines, guanidines, group I alkoxides, quaternary hydroxides, quaternary alkoxides, and alkoxide bases generated *in situ* by reaction between a halide anion and an epoxy moiety.

22. The liquid oligomeric composition, according to claim 20, wherein said base is chosen from the group consisting of diazabicycloundecene (DBU), diazabicyclo-nonene (DBN), and 1,1,3,3-tetramethyl guanidine.

23. The liquid oligomeric composition, according to claim 21, wherein said alkoxide is generated in-situ by reaction between a quaternary halide and an epoxide moiety.

24. The liquid oligomeric composition, according to claim 4, wherein said diacrylate is selected from the group consisting of:

ethylene glycol diacrylate, propylene glycol diacrylate,
diethylene glycol diacrylate, dipropylene glycol diacrylate,
triethylene glycol diacrylate, tripropylene glycol diacrylate,
tetraethylene glycol diacrylate, tetrapropylene glycol diacrylate,
polyethylene glycol diacrylate, polypropylene glycol diacrylate,
ethoxylated bisphenol A diacrylate,
bisphenol A diglycidyl ether diacrylate,
resorcinol diglycidyl ether diacrylate,
1, 3-propanediol diacrylate,
1, 4-butanediol diacrylate,
1, 5-pentanediol diacrylate,
1, 6-hexanediol diacrylate,
neopentyl glycol diacrylate,
cyclohexane dimethanol diacrylate,
ethoxylated neopentyl glycol diacrylate, propoxylated neopentyl glycol diacrylate,
ethoxylated cyclohexanedimethanol diacrylate, propoxylated cyclohexanedimethanol diacrylate,
acrylated epoxy diacrylates,

aryl urethane diacrylates, aliphatic urethane diacrylates, polyester diacrylates, and mixtures thereof.

25. The liquid oligomeric composition, according to claim 4, wherein said triacrylate is selected from the group consisting of:

trimethylol propane triacrylate,
glycerol triacrylate,

ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, tris (2-hydroxyethyl) isocyanurate triacrylate, ethoxylated glycerol triacrylate, propoxylated glycerol triacrylate, pentaerythritol triacrylate, aryl urethane triacrylates, aliphatic urethane triacrylates, melamine triacrylates, aliphatic epoxy triacrylates, epoxy novolac triacrylates, polyester triacrylates and mixtures thereof.

26. The liquid oligomeric composition, according to claim 4, wherein said tetraacrylate is selected from the group consisting of:

pentaerythritol tetraacrylate, ethoxylated pentaerythritol tetraacrylate, propoxylated pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, ethoxylated dipentaerythritol tetraacrylate, propoxylated dipentaerythritol tetraacrylate, aryl urethane tetraacrylates, aliphatic urethane tetraacrylates, melamine tetraacrylates, epoxy novolac tetraacrylates, and mixtures thereof.

27. The liquid oligomeric composition, according to claim 6, wherein said β -dicarbonyl donor compound having functionality = 2 is selected from the group consisting of:

ethyl acetoacetate, methyl acetoacetate, 2-ethylhexyl acetoacetate, lauryl acetoacetate, t-butyl acetoacetate, acetoacetanilide, N-alkyl acetoacetanilide, acetoacetamide, 2-acetoacetoxylethyl methacrylate, allyl acetoacetate, benzyl acetoacetate, 2, 4-pentanedione, 2, 4-hexanedione, 3, 5-heptanedione, isobutyl acetoacetate, and 2-methoxyethyl acetoacetate.

28. The liquid oligomeric composition, according to claim 6, wherein said β -dicarbonyl donor compound having functionality = 4 is selected from the group consisting of:

1,4-butanediol diacetoacetate,
1,6-hexanediol diacetoacetate,
neopentyl glycol diacetoacetate,
cyclohexane dimethanol diacetoacetate, and
alkoxylated bisphenol A diacetoacetate.

29. The liquid oligomeric composition, according to claim 6, wherein said β -dicarbonyl donor compound having functionality = 6 is selected from the group consisting of:

trimethylol propane triacetoacetate,
glycerin triacetoacetate, and
polycaprolactone triacetoacetates and alkoxylated derivatives thereof.

30. The liquid oligomeric composition, according to claim 6, wherein said β -dicarbonyl donor compound having functionality = 8 is pentaerythritol tetraacetoacetate and alkoxylated derivatives thereof.

31. The liquid oligomeric composition, according to claim 2, wherein said Michael addition reaction occurs in the presence of at least one non-reactive solvent.

32. The liquid oligomeric composition, according to claim 15, wherein said non-reactive solvent is selected from the group consisting of styrene, t-butyl styrene, α -methyl styrene, vinyl toluene, vinyl acetate, allyl acetate, allyl methacrylate, diallyl phthalate, $C_1 - C_{18}$ -methacrylate esters, dimethacrylates, and trimethacrylates.

33. The liquid oligomeric composition, according to claim 1, wherein said composition is shelf stable for more than one month and has residual pendant unsaturated acrylate groups.

34. The liquid oligomeric composition, according to claim 1, further comprising a stabilizing agent.
35. The liquid oligomeric composition, according to claim 34, wherein a preferred stabilizing agent comprises (N-nitroso-N-phenylhydroxylamine)₃Al.
36. The liquid oligomeric composition, according to claim 2, further comprising an acidifying agent.
37. The liquid oligomeric composition, according to claim 36, wherein said acidifying agent is chosen from a group consisting of phosphoric acids, carboxylic acids, acid half esters, and inorganic acid esters.
38. The liquid oligomeric composition, according to claim 36, wherein a preferred acidifying agent is selected from the group consisting of phosphate esters of 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, and 4-hydroxybutyl methacrylate.
39. The liquid oligomeric composition, according to claim 2, further comprising a monoacrylate.
40. The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is chosen from the group consisting of simple C₁ – C₁₈ acrylate esters, isobornyl acrylate (IBOA), tetrahydrofurfuryl acrylate (THFFA), 2-(2-ethoxy ethoxy) ethyl acrylate (EOEOEA), phenoxyethyl acrylate (PEA), hydroxyalkyl acrylate, monoalkyl polyalkylene glycol acrylate,

siloxane, silane or silicone acrylate, perfluoroalkyl acrylate, caprolactone acrylate, and mixtures thereof.

41. The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present from about 0 to about 50 mol %.

42. The liquid oligomeric composition, according to claim 2, further comprising a free-radical generator.

43. The liquid oligomeric composition, according to claim 42, wherein said free-radical generator comprises a peroxide.

44. The liquid oligomeric composition, according to claim 42, wherein said peroxide is selected from the group consisting of methyl ethyl ketone peroxide (MEKP), tert-butyl perbenzoate (TBPB), cumyl peroxide, and t-butyl peroxide.

45. The liquid oligomeric composition, according to claim 2, further comprising a photoinitiator.

46. A polymerized product comprising:

a liquid oligomeric composition comprising:

a multifunctional mercaptan; and

an organic soluble, ungelled, uncrosslinked, Michael addition polyacrylate reaction product, further crosslinked in the presence of a free-radical-generator.

47. The polymerized product, according to claim 46, wherein said free-radical generator is actinic light.

48. The polymerized product, according to claim 46, wherein said free-radical generator is a peroxide.
49. The polymerized product, according to claim 46, further comprising a photoinitiator.
50. A method of making a liquid oligomeric composition, wherein said oligomeric composition has pendant unsaturated acrylate groups, the method comprising:
reacting a multifunctional acrylate Michael acceptor and a β -dicarbonyl Michael donor in the presence of a strong base to form a Michael adduct;
adding an acidifying agent to said adduct in an amount at least stoichiometric with said base; and
admixing a multifunctional mercaptan.
51. A method of using a liquid oligomeric composition comprising:
providing a liquid oligomeric composition comprising:
a multifunctional mercaptan, and
an organic soluble, ungelled, uncrosslinked, Michael addition polyacrylate reaction product;
applying said oligomeric composition to a surface; and
curing said composition.
52. A method of using a liquid oligomeric composition, according to claim 51, wherein curing comprises providing a free-radical generator.

53. A method of using a liquid oligomeric composition, according to claim 52, wherein said free-radical generator is actinic light.

54. A method of using a liquid oligomeric composition, according to claim 52, wherein curing comprises reacting said composition under base catalyzed conditions.

55. A method of using a liquid oligomeric composition, according to claim 52, wherein said composition further comprises at least one additive.

56. A method of using a liquid oligomeric composition, according to claim 55, wherein said additive is selected from the group consisting of pigments, gloss modifiers, flow and leveling agents and other additive as appropriate to formulate coatings, paints, laminates, sealants, adhesives and inks.

57. The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present from about 0 to about 25 mol %.

58. The liquid oligomeric composition, according to claim 39, wherein said monoacrylate is present from about 0 to about 12.5 mol %.